

Increased Oxygen Recovery from Sabatier Systems Using Plasma Pyrolysis Technology and Metal Hydride Separation

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State-of-the-art life support carbon dioxide (CO₂) reduction technology is based on the Sabatier reaction where less than 50% of the oxygen required for the crew is recovered from metabolic CO₂. The reaction produces water as the primary product and methane as a byproduct. Oxygen recovery is constrained by the limited availability of reactant hydrogen. This is further exacerbated when Sabatier methane (CH₄) is vented as a waste product resulting in a continuous loss of reactant hydrogen. Post-processing methane with the Plasma Pyrolysis Assembly (PPA) to recover hydrogen has the potential to dramatically increase oxygen recovery and thus drastically reduce the logistical challenges associated with oxygen resupply. The PPA decomposes methane into predominantly hydrogen and acetylene. Due to the highly unstable nature of acetylene, a separation system is necessary to purify hydrogen before it is recycled back to the Sabatier reactor. Testing and evaluation of a full-scale Third Generation PPA is reported and investigations into metal hydride hydrogen separation technology is discussed.

Nomenclature

C	=	Constant
CM	=	Crew Member
CDRA	=	Carbon Dioxide Removal Assembly
CRA	=	Carbon Dioxide Reduction Assembly
H	=	Enthalpy
HS	=	Hamilton Sundstrand
Int	=	Integrated
ISS	=	<i>International Space Station</i>
MSFC	=	Marshall Space Flight Center

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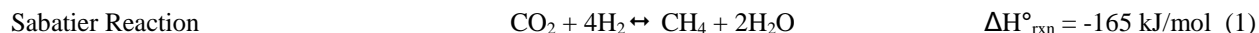
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MTL	=	Moderate Temperature Loop
OGA	=	Oxygen Generation Assembly
P	=	Pressure
PPA	=	Plasma Pyrolysis Assembly
R	=	Universal Gas Constant
SA	=	Stand Alone
SDU	=	Sabatier Development Unit
SmLPM	=	Standard milliliters Per Minute
T	=	Absolute Temperature
UHP	=	Ultra High Purity
UTAS	=	UTC Aerospace Corporation
W	=	Watts

I. Introduction

HUMAN life support systems on the *International Space Station (ISS)* include a number of technologies to continuously provide breathable air to the crew. The Trace Contaminant Control System removes harmful volatile organic compounds and other trace contaminants from the circulating air. The Carbon Dioxide Removal Assembly (CDRA) removes metabolic carbon dioxide (CO₂) and returns humidified air to the cabin. The Oxygen Generation Assembly (OGA) electrolyzes water to produce oxygen for the crew and hydrogen (H₂) as a byproduct. The Carbon Dioxide Reduction Assembly (CRA), the most recently added technology, compresses and stores CO₂ from the CDRA until hydrogen is available from the OGA. The CO₂ and H₂ are then fed to a Sabatier reactor for reduction to form water and methane as shown in Equation 1.

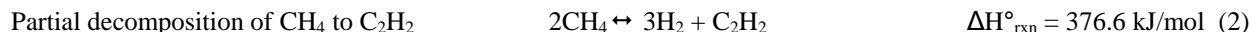


The water product is condensed out of the product stream and recycled back to the Water Purification Assembly for crew use or to produce additional oxygen in the OGA. The methane is vented overboard as a waste product. For future long-duration missions or missions beyond low Earth orbit, hydrogen may be recovered from methane and recycled back to the CRA to produce additional water and, by producing additional water, increase total oxygen recovery.

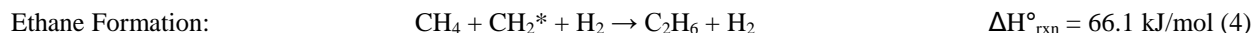
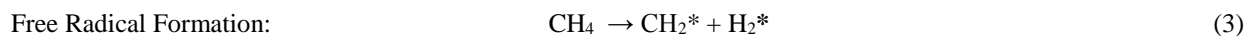
Two technologies, the Plasma Pyrolysis Assembly (PPA) and metal-hydride hydrogen separation/purification, are presented here to address the need for hydrogen recovery from Sabatier-produced methane.

II. Background

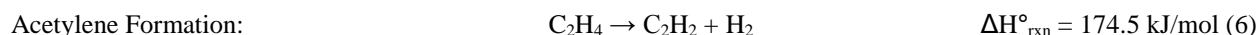
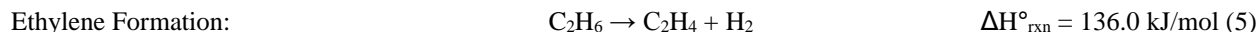
The Plasma Pyrolysis Assembly (PPA) is one potential methane post-processor for Sabatier-produced methane. Extensive testing on a sub-scale systems has been reported previously.^{1,2,3,4} Briefly, this technology targets the conversion of methane to H₂ and acetylene (C₂H₂) as shown in Equation 2.



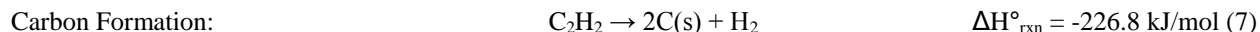
Decomposition of methane occurs through the formation of free radicals as shown in Equations 3 and 4.⁵



Where “*” denotes a radical. Each product reacts in turn with the radicals to form the next product as shown in Equations 5 and 6.



If sufficient energy is provided, the reaction will proceed to complete conversion of methane to solid carbon and hydrogen, as shown in Equation 7.



The PPA provides the considerable energy required for methane conversion by generating a plasma using microwave power. Hydrogen is fed to the reactor in addition to CH_4 to limit CH_4 decomposition to acetylene rather than to carbon. When operated as a stand-alone unit with bottled gas feeds of CH_4 and H_2 , the gas effluent from the PPA generally consists of H_2 , unreacted CH_4 , and C_2H_2 with trace quantities of ethylene and ethane. When the PPA is operated while integrated with a Sabatier system, the methane from the Sabatier is saturated with water vapor. The mixture of water vapor and methane provides the potential to form other products (commonly known as steam reforming) as shown in Equations 8 and 9 below.



This saturated feed stream results in a PPA gas effluent containing H_2 , unreacted CH_4 , C_2H_2 , carbon monoxide (CO), and water vapor with trace quantities of ethylene and carbon dioxide.³ Both operational modes also result in small quantities of solid carbon. The first generation system was designed to process methane at a flow rate equivalent to ~1/2 crew member (CM). In 2012, a second generation system was designed and delivered to the Marshall Space Flight Center (MSFC) to process methane at a 1-CM rate.⁶ Additionally, this system was designed for improved energy efficiency, better C_2H_2 selectivity, greater methane conversion, and reduced carbon production. A system architecture incorporating the PPA was proposed and is shown slightly modified in Figure 1. This architecture includes a hydrogen purification assembly (originally called an Acetylene Purification Assembly) that enables the PPA H_2 product to be purified before recycling back to the Sabatier and PPA.

In 2013 the latest generation of PPA was delivered to MSFC. The 3rd Generation PPA utilizes a cylindrical reactor design to process methane at up to a 5-CM rate. In addition, a regenerable carbon trap was included to capture byproduct carbon.⁶

The results of initial testing of the 3rd Generation PPA are discussed here.

Extracting a pure, dry H_2 product from the PPA's effluent gases that is suitable for use as a CO_2 reduction process reactant is a key step toward achieving the resource recovery needed for exploration missions. Industrially, H_2 separation from gas mixtures is accomplished by the following methods:⁷

- 1) Cryogenic separation
- 2) Polymer membrane diffusion
- 3) Metal hydride separation
- 4) Solid polymer electrolytic cell separation
- 5) Pressure swing adsorption
- 6) Catalytic purification
- 7) Palladium membrane diffusion

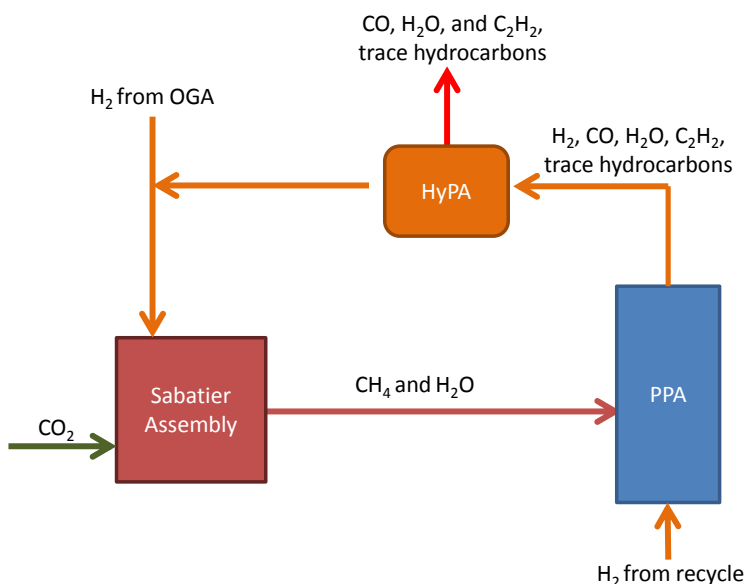


Figure 1. Sabatier and PPA architecture.

All of these methods are capable of >70% H_2 recovery and delivering >90% purity. The methods typically applied to small scale separations include polymer membrane diffusion, metal hydride separation, solid polymer electrolytic separation, catalytic purification, and palladium membrane diffusion while cryogenic separation and pressure swing

adsorption processes are typically applied to large scale separations. Considering the five methods best suited for small scale applications, the metal hydride separation, solid polymer electrolytic, and palladium membrane diffusion processes have the greatest potential for separating a dry, purified H₂ product from the PPA effluent gases. Polymer membrane diffusion suffers from selectivity issues that can allow water, CO, and other constituents in the PPA effluent gases to diffuse across the membrane along with H₂. Cryogenic separation requires a high power demand to condition the gases to promote fractional condensation and may require further purification steps to remove CO₂ and water. These characteristics make polymer membrane diffusion and cryogenic separation processes less desirable for the PPA effluent gas separation.

Challenges also exist for the three methods of most interest for separating H₂ from the PPA effluent gases. These challenges include separation efficiency variation, poisoning by PPA effluent gas constituents, and the temperature and pressure conditions necessary for the process technology to perform properly. The desire is to employ a robust process technology that is compatible with the PPA's effluent gas composition and operate efficiently at a temperature range below the C₂H₂ autoignition temperature (325 °C) and in the pressure range between 14.2 kPa and 101.3 kPa.

First, metal hydride separation has a wide range of separation efficiency compared to solid polymer electrolytic and palladium membrane diffusion processes. The key is to select a metal hydride alloy that is competitive with the >95% separation efficiency that can be achieved by solid polymer electrolytic and the nearly 99% separation efficiency reported for palladium membrane diffusion processes. A variety of metal hydride alloys have been studied in the literature. The alloys of most importance for the PPA application include a variety of lanthanum-nickel (La-Ni) combinations.⁸ A lanthanum-nickel-aluminum alloy arranged in a packed bed configuration was evaluated to provide >95% separation efficiency from an industrial gas mixture consisting of 60.8% H₂, 20.0% N₂, 12.1% CH₄, 3.2% argon (Ar), and 3.9% ammonia (NH₃).⁹

Second, the metal hydride and palladium membrane processes can be poisoned or degraded in the presence of some of the PPA's effluent gas constituents. For example, metal hydride separation processes can be degraded by oxygen (O₂), nitrogen (N₂), CO, CO₂, sulfur, and water. Methods have been studied to reduce metal hydride and palladium membrane susceptibility to poisons. Encapsulating a nanocomposite hydride alloy in a porous polymethylmethacrylate (PMMA) matrix has been shown to protect a magnesium (Mg) hydride alloy from poisons.¹⁰ Nanostructured surface coatings and surface fluorination have also been reported to improve metal hydride alloy susceptibility to poisoning by water, CO, CO₂, and O₂.^{11,12,13} Some success has been reported for regenerating a metal hydride in vacuum at 160 °C.¹⁴ So, there is the potential for in-situ regeneration of a degraded metal hydride system. Similarly, palladium membrane diffusion processes can be impaired by the presence of hydrocarbons, CO, and water in the process gas. Palladium membrane processes operating >450 °C are susceptible to deactivation by hydrocarbons and coking while membrane embrittlement and CO poisoning are reported to be worse at temperatures <300 °C and <150 °C, respectively.¹⁵ This makes operating a palladium membrane process at any temperature unviable due to the inevitable fouling. Comparatively, solid polymer electrolytic processes are sensitive to sulfur which can poison catalytic electrodes making this process the most compatible with the PPA's effluent gas composition due to the absence of sulfur compounds in the PPA effluent.

Third, the palladium membrane diffusion process and some metal hydride alloys operate most effectively at high temperature and pressure conditions. Palladium-silver (PdAg) membrane alloys consisting of 23% Ag are the most common. Operating temperatures range between 450 °C and 600 °C.¹⁶ Other palladium alloys that include yttrium (Y), ruthenium (Ru), copper (Cu), and indium (In) have been studied with a Pd-In-Ru alloy having optimum operating conditions above 350 °C and 1.8 MPa.¹⁷ Palladium-copper membranes have been studied for operating conditions of 350 °C to 900 °C and 2.6 MPa hydrogen pressure.¹⁸ Overall, the palladium membrane processes operate at both temperatures and pressures that are not compatible with the desired PPA effluent gas conditions. Metal hydride alloys can be selected for operating over a variety of temperature and pressure conditions. Many alloys are available for operating in the -23 °C and 380 °C range.¹⁹ Similarly, a number of metal hydride alloys have been shown to have favorable performance near 20 °C and 101.3 kPa.²⁰ These alloys are typically lanthanum-based.

Considering the technical challenges and compatibility with the PPA's effluent gas composition and operating conditions, metal hydride separation and solid polymer electrolytic processes appear to have the greatest potential for the H₂ recovery application based on industrial applications. Further research on solid polymer electrolytic processes applied to H₂ separation for the PPA effluent is ongoing and reported elsewhere.²¹ A sorbent-based approach, useful for small scale applications, thus not traditionally used in industrial process, is also under development and reported elsewhere.²² Metal hydrides are evaluated in greater detail here.

III. Methods

This paper reports the results of testing of the 3rd Generation PPA and provides a discussion of metal hydrides as an option for hydrogen separations. The PPA was tested in two modes: stand-alone and integrated. The methods used in this testing are provided below. The discussion of metal hydrides is based on a comprehensive literature review of metal hydride research and information obtained from the specified vendors.

A. 3rd Generation PPA Hardware Facility Integration

The 3rd Generation PPA is installed in the Environmental Chamber (E-Chamber) at NASA's Marshall Space Flight Center as shown in Figure 2. The integration design includes the option to provide gas feed to the PPA from either purified bottled sources or directly from the UTC Aerospace Corporation (UTAS) Hamilton Sundstrand (HS) Sabatier Development Unit (SDU). The PPA was delivered with a chiller and coolant loop to provide independent cooling to the reactor and microwave water load. To more closely mimic *ISS* performance, the original coolant loop was removed and the PPA was plumbed to the E-Chamber Moderate Temperature Loop (MTL) that provides coolant at ~15°C.

B. 3rd Generation PPA Stand-Alone Performance Testing

The purpose of stand-alone testing was to verify that no changes to the system had occurred since final testing at Umpqua Research Company and to generate baseline performance data from which all other testing may be compared. Stand-alone testing was performed by providing ultra high purity (UHP) hydrogen and methane from pressurized bottles (Airgas) to the PPA and evaluating the conversion performance at methane feed rates equivalent to those produced by a crew of 1, 2, 3, 4, and 5. Hydrogen feed was set to four times the total methane feed (molar). Microwave power and tuning was set to values identified by Umpqua during development to provide the optimum combination of methane conversion and acetylene selectivity at each production rate. Reactor pressure was set to 50 torr during start-up and maintained at 110 torr during operation. Cleaning cycles of the reactor and carbon trap were conducted when the pressure drop across the carbon trap exceeded ~70 torr. Performance metrics included total methane conversion (% CH₄ Conversion), methane conversion to C₂H₂ (% CH₄ Conv to C₂H₂), methane conversion to C₂H₄ (% CH₄ Conv to C₂H₄), and hydrogen recovery (% H₂ Recovery_SA). The "SA" in "% H₂ Recovery_SA" refers to the "Stand-Alone" operation of the PPA where hydrogen is recovered from methane only. It should be noted that when calculating total moles of each product, carbon was assumed to be negligible. The definition of each metric is provided below.



Figure 2. 3rd Generation PPA (blue) integrated into E-Chamber. HS SDU (silver) show immediately to the left of the PPA. PPA integrated to enable either stand-alone or integrated operation.

$$\% \text{ CH}_4 \text{ Conversion} = \frac{\text{molesCH}_4 \text{ Converted}}{\text{molesCH}_4 \text{ Fed}} * 100 \quad (10)$$

$$\% \text{ CH}_4 \text{ Conv to C}_2\text{H}_2 = \frac{\text{molesC}_2\text{H}_2 \text{ Produced}}{\text{molesCH}_4 \text{ Fed}} * 100 \quad (11)$$

$$\% \text{ CH}_4 \text{ Conv to C}_2\text{H}_4 = \frac{\text{molesC}_2\text{H}_4 \text{ Produced}}{\text{molesCH}_4 \text{ Fed}} * 100 \quad (12)$$

$$\% \text{ H}_2 \text{ Recovery_SA} = \frac{3 * \text{molesC}_2\text{H}_2 \text{ Produced} + 2 * \text{molesC}_2\text{H}_4}{2 * \text{molesCH}_4 \text{ Fed}} * 100 \quad (13)$$

C. 3rd Generation PPA Integrated Performance Testing

The purpose of integrated testing was to evaluate the performance of the 3rd Generation PPA with a Sabatier-methane feed stream. During testing, the Sabatier was operated at CO₂ feed rates equivalent to 2-crew member (CM), 3-CM, and 4-CM production rates and an H₂:CO₂ ratio of 4.5 to ensure all CO₂ was reacted. The methane product was fed directly to the PPA. The Sabatier condensing heat exchanger uses E-chamber air as the coolant resulting in a gas stream dewpoint slightly higher than the ambient temperature. Total hydrogen fed to the PPA was four times (molar) the total methane fed to the reactor. A portion of this was provided with the methane as unreacted Sabatier product. The balance was provided from pressurized bottles of UHP hydrogen. The PPA performance at these feed set points was evaluated at the optimum power levels identified by Umpqua, 100W lower than optimum, and 100W and 200W higher than optimum. Reactor pressure was set to 110 torr during operation. Performance metrics included total methane conversion, methane conversion to C₂H₂, and methane conversion to C₂H₄, all as defined in Equations 10-12, above. Additional integrated testing metrics included methane conversion to CO (% CH₄ Conv to CO), methane conversion to CO₂ (% CH₄ Conv to CO₂), and hydrogen recovery from methane (% H₂ Recovery_Int). It should be noted that in the case of the hydrogen recovery from methane, the calculation excludes the H₂ produced from water vapor. The “_Int” refers to Integrated operation of the PPA with the Sabatier. Each of the additional metrics is defined below. Again, all calculations assume that carbon formation is negligible.

$$\% \text{ CH}_4 \text{ Conv to CO} = \frac{\text{moles CO Produced}}{\text{moles CH}_4 \text{ Fed}} * 100 \quad (14)$$

$$\% \text{ CH}_4 \text{ Conv to CO}_2 = \frac{\text{moles CO}_2 \text{ Produced}}{\text{moles CH}_4 \text{ Fed}} * 100 \quad (15)$$

$$\% \text{ H}_2 \text{ Recovery_Int} = \frac{3 * \text{moles C}_2\text{H}_2 \text{ Produced} + 2 * \text{moles C}_2\text{H}_4 + \frac{1}{2} * \text{moles CO} + \frac{3}{2} * \text{moles CO}_2}{2 * \text{moles CH}_4 \text{ Fed}} * 100 \quad (16)$$

IV. Results and Discussion

The 3rd Generation PPA performance was demonstrated for a range of operational rates both as a stand-alone unit and integrated with the SDU. The results of this testing is provided below. A literature review of metal hydrides as a potential approach to PPA hydrogen recycle was evaluated. A discussion of the findings is provided below.

A. 3rd Generation PPA Stand-Alone Testing Results and Discussion

PPA stand-alone testing was conducted at 1-CM, 2-CM, 3-CM, 4-CM, and 5-CM. During development of the 3rd Generation PPA, greater than 90% conversion of methane was targeted for processing rates of 4-CM and lower. Data collected at 5-CM was collected to gauge performance at off-nominal conditions. Figure 3 shows the data from testing at NASA, which closely matched the performance observed by Umpqua and demonstrated the targeted

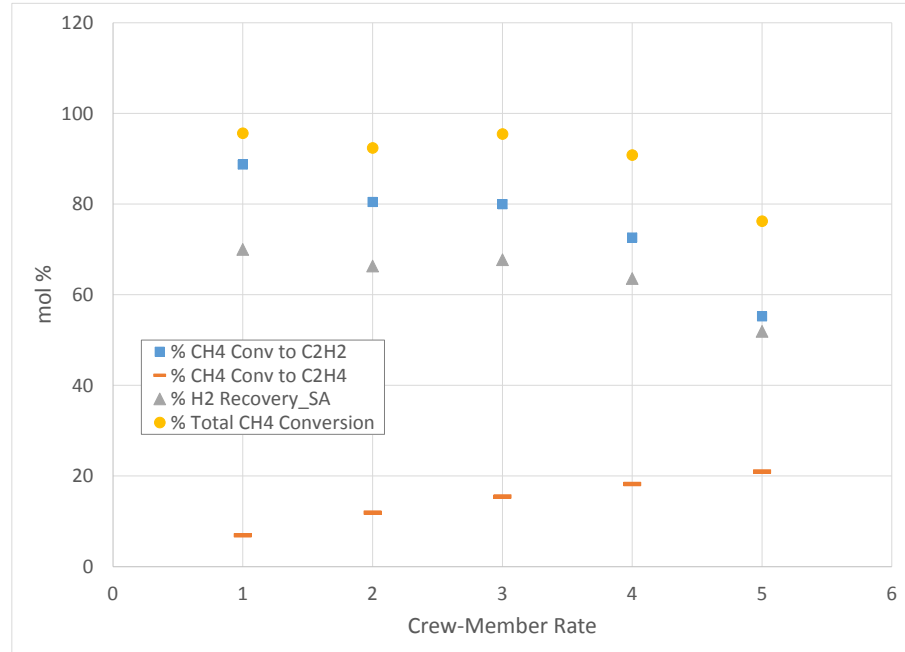


Figure 3. Performance of 3rd Generation PPA during stand-alone testing.

performance. Additionally, conversion of methane to acetylene and hydrogen (the desired products) was above 80% for processing rates of 1-, 2-, and 3-CM. For 4-CM, the conversion was only slightly lower. This resulted in hydrogen recovery of more than 60% for the processing rates for which the hardware was designed.

As processing rate increased, a downward trend was observed in conversion of methane to acetylene. Simultaneously, methane conversion to ethylene was observed to increase.

Hydrogen recovery and total methane conversion decreased from 1-CM to 2-CM due to the decrease in conversion to acetylene, but increased at 3-CM due to the significant increase in production of ethylene. At 4-CM and 5-CM all parameters except ethylene production decreased. Recall from Equation 6 above, that ethylene is a pre-cursor to acetylene in methane decomposition. These trends may be explained in

several ways. First, it is possible that insufficient power is available to fully convert the methane to acetylene, resulting in ethylene production instead. However, when looking at reflected power levels (the quantity of un-used energy in the system) in Figure 4, only 5-CM appears to have significant energy inefficiencies. Second, it is possible that the total residence time of the gas is not adequate to fully convert the methane to acetylene, leaving the partially converted ethylene instead of the desired acetylene product. This appears to be the more likely cause given the consistent increase in ethylene production. There are several possible options to address this challenge. First would be to increase the operational pressure to increase the total residence time of the ionized species. This could introduce potential safety challenges were there to be an air leak during operation, so a thorough safety analysis would be required before this could be accomplished. A second option would be to increase the total power of the system. This also is not a favorable option given the already considerable energy required for operation, the potential to increase solid carbon production, the anticipated increase in energy inefficiency, and the likely limited benefit given the 5-CM data. A third option is to fine-tune the microwaves as they enter the reactor chamber. Umpqua's hardware allows for this type of tuning designed to minimize the reflected power. The fourth option, and the most likely to result in the best results, is to do a combination of the above. Modest improvements can be expected with a small increase in reactor pressure, an increase in total microwave power, and fine-tuning of the microwave. Even without these modifications, the 3rd Generation PPA clearly meets the targeted performance and currently recovers over 60% of the hydrogen from Sabatier methane (with a 75% theoretical maximum) at the 4-CM processing rate.

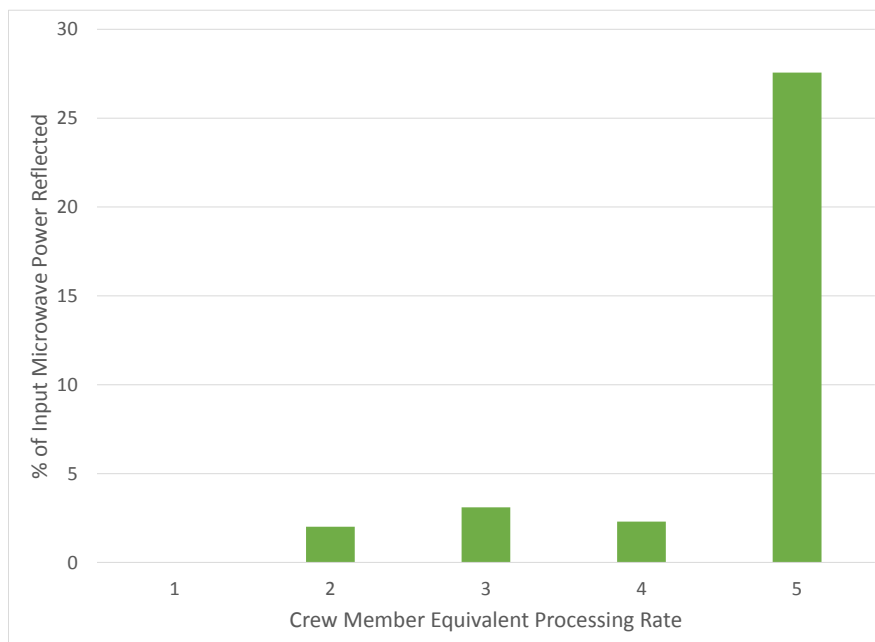


Figure 4. Percentage of Input Power Reflected During Operation of the 3rd Gen PPA in Stand-Alone Testing.

B. 3rd Generation PPA Integrated Testing Results and Discussion

The 3rd Generation PPA was integrated with the Sabatier to evaluate the performance when fed a saturated methane stream containing unreacted hydrogen. Initial testing repeated the data points from stand-alone testing to directly compare performance between pure methane and the Sabatier methane stream containing water vapor and hydrogen. As can be seen in Figure 5, the presence of the water vapor and hydrogen in the methane feed dramatically reduced the performance of the system. At the nominal production rate of 4-CM, the total methane conversion decreased from ~90% to ~66%. Similarly, total conversion of methane to acetylene decreased from ~73% to ~43%.

This data suggests that much of the energy in the system that went to convert methane to acetylene in stand-alone testing was dedicated instead to ionizing the water vapor. This is further demonstrated by observing the methane conversion to carbon monoxide. No CO was observed in stand-alone testing due to the absence of oxygenated compounds for reaction. However, the presence of water vapor provides the reactant to proceed via Equation 9 when the Sabatier product is fed directly to the PPA. Interestingly, there was very little difference in percent conversion of methane to ethylene between the two tests. With more of the microwave energy going to ionize water, it would be expected that the conversion to ethylene would be considerably greater in the integrated test than in the stand-alone test, particularly given the decrease in acetylene production and the fact that the energy required to produce CO

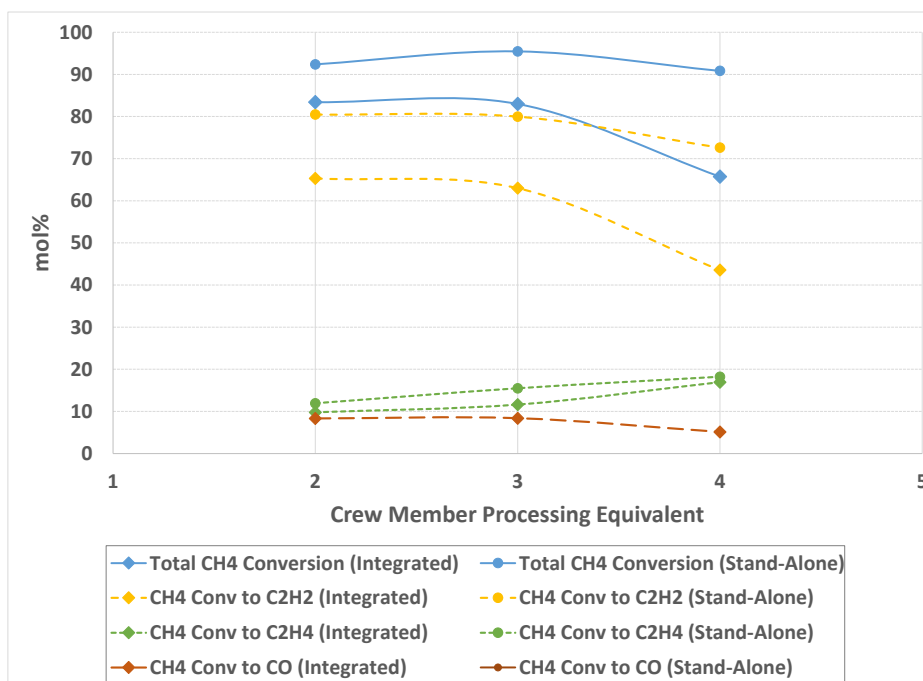


Figure 5. Comparison of Stand-Alone versus Integrated Performance of the 3rd Generation PPA.

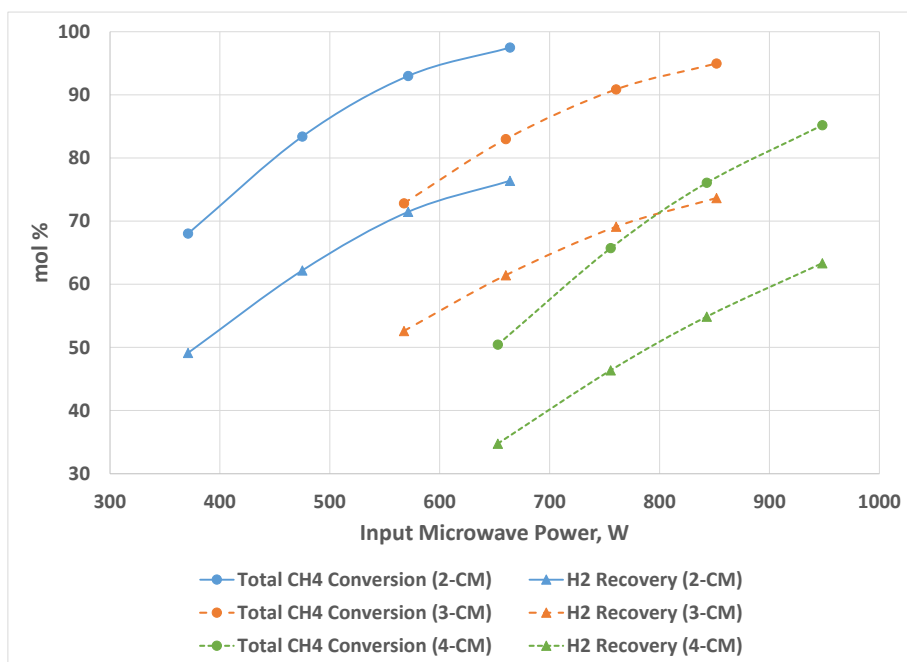


Figure 6. Demonstrated Performance of the 3rd Generation PPA when Integrated with the Sabatier at 2-CM, 3-CM, and 4-CM Processing Rates.

is considerably greater than the energy required to produce ethylene. This unexpected result suggests thermodynamic limitations and/or mass transport limitations in the reactor. If the system were thermodynamically limited, the conversion to ethylene would be limited by thermodynamic equilibrium at the gas temperature. This would correlate to the observed ethylene conversion in both the integrated and stand-alone tests. Additionally, this would correlate to the combination of increased CO production and decreased acetylene conversion given that the reactions have similar enthalpy's of reaction, with acetylene production requiring slightly less energy to achieve. A second possibility is that the system is limited by mass transport. Total mass and volume flowing through the system increases with the introduction of the water vapor into the system. This results in a lower residence time for each reactant molecule. Given that the production of acetylene from methane is dependent on the formation of several radicals and intermediates, it follows that a shorter residence time would result in a decrease in conversion.

While the trends in the data can be explained, of more interest is how this will affect an integrated life support system. Stand-alone performance of the PPA suggests >90% methane conversion at a 4-CM rate. However, when water vapor and hydrogen are introduced with the methane, the conversion decreases to 66%. Hydrogen recovery decreases from ~60% to ~46%, as seen in Figure 6. These values must be improved to justify implementation of this system into an ISS flight experiment or future surface mission. In an effort to examine the affect of the total

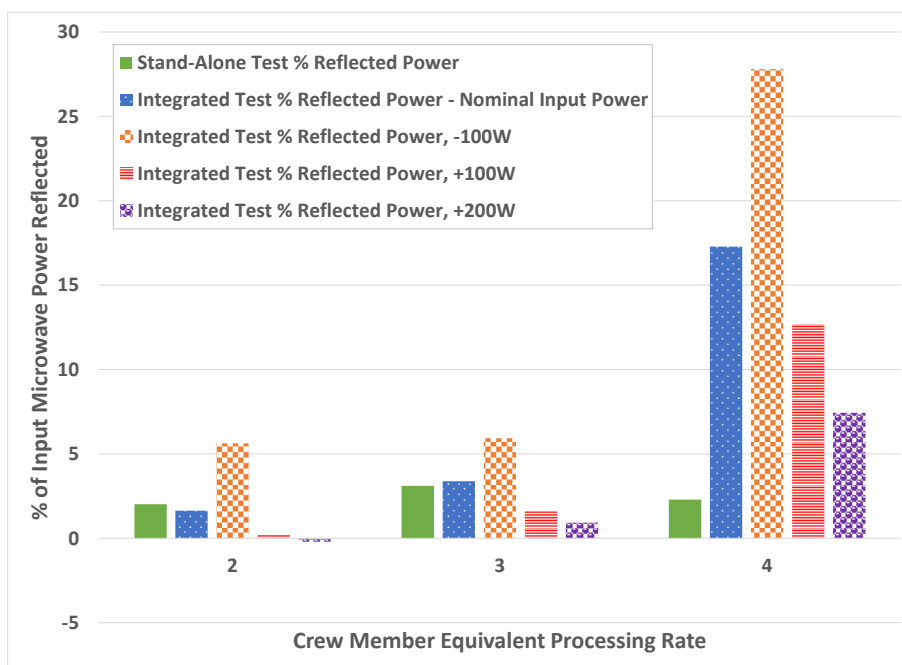
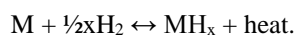


Figure 7. Total Percentage of Microwave Power Reflected during Stand-Alone and Integrated Testing.

microwave power on the the metrics, the microwave power was varied for 2-CM, 3-CM, and 4-CM process rates. In order to achieve the desired >90% methane conversion, the power at 2-CM and 3-CM had to be increased by 100W. At 4-CM, an increase of 200W was still not sufficient to achieve the 90% conversion. Extrapolation of the data suggests that this could be achieved at ~1000W (~250W greater than nominal). However, another thing to consider is the reflected power. High reflected power suggest either insufficient gas to ionize or inadequate tuning of the available microwaves. Figure 7 shows the percentage of the total input power that was reflected. The total percentage reflected power for the 4-CM integrated data points is significantly higher than the stand-alone test point. Better tuning of the reactor during operation at this processing rate could have a dramatic affect on this value and a corresponding effect on the methane conversion and hydrogen recovery. Thus, a combination of increase microwave power and improved tuning could result in integrated performance more similar to the stand-alone performance.

C. Metal Hydride Evaluation for PPA Hydrogen Recycling

A metal hydride is formed when H₂ reacts with a metal or metal alloy to form a chemical compound. The reversible reaction between the solid and H₂ is reversible and is characterized by the general reaction,



In this reaction, the hydrogen becomes reversibly bound in the crystalline structure of the metal alloy. A vapor pressure relationship exists between the hydrogen in the gaseous and solid phases and the equilibrium condition can be expressed as functions of pressure, temperature, and composition. For a particular temperature, a pressure plateau occurs at the combined temperature and pressure condition that favors the hydride formation reaction. Many metal

hydrides absorb and desorb H_2 at temperatures and plateau pressures that are suitable for applying to the PPA effluent gas separation challenge. The plateau pressure is highly dependent on temperature according to a van't Hoff relationship,

$$\ln(P/P_o) = \Delta H/RT + C.$$

In the van't Hoff relationship, T is the absolute temperature, ΔH is the enthalpy change per mole of H_2 , R is the universal gas constant, and C is a constant related to the entropy change of the reaction. As the hydride formation reaction progresses, energy is liberated and must be removed to avoid a temperature increase in the reactor. Likewise, to release H_2 , energy must be added to the reactor to increase the temperature. Because the process is sensitive to temperature the process equipment must be well engineered to promote efficient energy transfer during the absorption and desorption cycles. The absorption and desorption reactions can exhibit hysteresis such that the plateau pressures can vary. Due to hysteresis the absorption and desorption temperatures will vary for a given plateau pressure.

Metal hydrides are characterized by high volumetric packing density. For instance, a $LaNi_5H_{6.7}$ hydride has a volumetric density of 7.6×10^{22} atoms H/ml which is nearly 81% greater than the liquid H_2 which has a volumetric density of 4.2×10^{22} atoms H/ml.¹⁸ The advantage in volumetric density is particularly useful for storage applications.

Spacecraft Applications

Previous metal hydride-based applications considered by NASA have focused on long term storage, refrigeration cycles, and capturing cryogenic boil-off. These applications are very different from the continuous separation and purification process needed for PPA effluent gas separation. Early work considered metal hydrides to store hydrogen fuel. An investigation for metal hydride-based low temperature refrigeration and long-term storage was conducted in the late 1980s for the Marshall Space Flight Center.²³ During early ISS development, metal hydride storage was considered for providing high purity carrier gas for analytical instruments and experiment payloads. Hydrogen storage using a commercially-available storage unit containing HY-STOR[®] alloy (Ergenics, Inc.) was considered for this purpose. A storage container based on a lanthanum-nickel ($LaNi_5$) alloy was sized for storing and delivering 14 grams/day of H_2 to experiment payloads.²⁴ It was proposed that the metal hydride storage canister could be recharged with H_2 produced by the water electrolysis-based oxygen generation process. Similar to these proposed applications aboard the ISS, a metal hydride storage unit was used for the 1997-launched Cassini-Huygens mission to Saturn. The two metal hydride storage containers provided by Ergenics, Inc. were filled with 58 grams of cerium-free mischmetal-nickel ($MmNi_5$) alloy and stored 0.86 grams (9.6 standard Liters) each of hydrogen. The high purity H_2 was used for the gas chromatograph-mass spectrometer aboard the Huygens probe that measured atmospheric composition as it descended to the surface of Saturn's moon, Titan, in 2005.²⁵ The feasibility for cryogenic boil-off capture was assessed by Ergenics, Inc. for the Kennedy Space Center.²⁶ None of these applications have been implemented aboard a crewed spacecraft.

Metal Hydride-based Separation Process Considerations

Although a cyclic, continuous metal hydride-based separation process has not been considered or developed by NASA, such a process is described for separating H_2 from industrial waste gas streams.²⁷ This process was based on fixed beds of $LaNi_5$ alloy in pellet form contained in shell-in-tube reactor beds to facilitate heat transfer. The process consisted of three batch processing stages—absorption, desorption, and conditioning. Because each processing stage possesses different kinetics that are dictated by heat transfer, three reactors were used to accommodate the three processing stages and provide a continuous process. This three-stage process is amenable to adaptation to the PPA effluent gas separation. Successfully adapting the process to the PPA application requires selecting a durable metal hydride alloy that is compatible with the PPA effluent gas composition. The pressure plateau condition must exist within the desired PPA effluent gas temperature and pressure conditions. Characteristics of a suitable metal hydride alloy are the following:

- 1) Fast reaction kinetics at the PPA effluent gas temperature and pressure conditions.
- 2) Compatible with the PPA effluent gas composition.
- 3) Cyclically stable relative to separation or disproportionation of the metal species.
- 4) Low volume expansion and pellet attrition during cycling.

The PPA effluent gas temperature and pressure conditions are a primary discriminator for selecting a metal hydride alloy. The temperature determines the pressure plateau through which the hydrogen absorption-desorption process occurs. Suitable metal hydride alloys are intermetallic compounds in the form of AB_x where A is a strongly hydride-forming metal and B is a weakly hydride-forming metal. The alloy may be binary or multi-component. A common

alloy is $\text{LaNi}_5\text{H}_{6.5}$. This alloy has a 1.49 weight percent maximum hydrogen capacity and a 1.28 weight percent reversible capacity. Although possessing fast kinetics, this alloy degrades at temperatures $>77^\circ\text{C}$. The adsorption-desorption pressure is 180 kPa at 25°C .²⁸ Multicomponent alloys with the AB_5 form such as $\text{LaNi}_{4.7}\text{Al}_{0.3}\text{H}_{6.0}$ and $\text{LaNi}_{4.8}\text{Sn}_{0.2}\text{H}_{6.0}$ have favorable kinetics and better resist degradation compared to $\text{LaNi}_5\text{H}_{6.5}$. The $\text{LaNi}_{4.7}\text{Al}_{0.3}\text{H}_{6.0}$ alloy has a absorption-desorption pressure of 40.5 kPa at 25°C .²⁹ Comparatively, the $\text{LaNi}_{4.8}\text{Sn}_{0.2}\text{H}_{6.0}$ alloy has an absorption-desorption pressure of 50 kPa at 25°C and a 1.40 weight percent maximum hydrogen capacity and a 1.24 weight percent reversible hydrogen capacity.³⁰ A commercial alloy, Hydralloy C15 (GfE) has been shown to possess an absorption-desorption pressure of 101.3 kPa at 10°C . The hydrogen storage capacity was up to 1.5 weight percent.³¹

Multicomponent alloys are reported to be more durable over a greater range of thermal cycles. For example, the reversible hydrogen capacity of LaNi_5 alloy is shown to degrade by 56% over 500 thermal cycles between 22°C and 237°C . The degradation, attributed to disproportionation of the alloy, is immediate and is nearly linear. In comparison, the reversible hydrogen capacity of a $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy has been shown to degrade by approximately 6% over 1,300 thermal cycles over the same temperature range.³² Fortunately, degradation due to disproportionation is minimal near 21°C . Therefore, the desire to operate the PPA hydrogen separation process near 21°C should have minimal reversible hydrogen capacity degradation. It is noted that the degradation that results from disproportionation can be reversed using a vacuum annealing process at $>327^\circ\text{C}$. Therefore, periodic heating and exposure to space vacuum can be used to regenerate the metal hydride alloy. Vacuum annealing may be incorporated as a process stage if desired.

Metal Hydride Separation Process Preliminary Size and Power Estimates

Using a $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy as a basis and assuming at least 1.2 weight percent reversible hydrogen capacity, the daily 855 grams (424 moles) H_2 produced by the PPA require approximately 63.3 kg of alloy. However, if a packed bed of alloy is sized to absorb H_2 for one hour, then the quantity of alloy is approximately 2.6 kg. Using three fixed beds containing 2.6 kg each operating cyclically then requires a total of 7.8 kg alloy. Assuming that structural components add another 20% to the mass, then the estimated system mass is approximately 10 kg.

By operating closer to 20°C , degradation by disproportionation can be minimized. If the reported 6% hydrogen capacity loss over 1,300 cycles is assumed to be a worst case, then subjecting the beds to vacuum annealing every 160 days may be prudent or an additional 14% alloy mass may be included to extend the period between vacuum annealing cycles to one year. Including the additional alloy mass increases the estimated hydride system mass to 11 kg.

Alloy poisoning by water, CO_2 , and CO must be evaluated under PPA effluent gas conditions to understand their impact. Hydrogen storage capacity losses of 10.7% has been reported for an AB_5 metal hydride alloy after 600 cycles.³³ Carbon dioxide and CO_2 impurities were present at ~ 200 ppm which is substantially lower than the CO concentration in the PPA effluent gases. Therefore it is possible that poisoning may occur more rapidly for the PPA application. The capacity was recovered by vacuum annealing at 160°C . Tolerance to poisoning by water will need to be evaluated at the PPA effluent gas conditions. Modifying AB_5 alloys with palladium and fluoride have been shown to greatly improve tolerance to poisoning by water and other compounds.³⁴

The enthalpy change for the $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy during absorption is -32.8 kJ/mole H_2 .³⁵ Therefore, the average energy removal during an absorption cycle is 161 Watts while a similar amount of energy must be added to the desorbing bed to liberate the H_2 . Maintaining a consistent temperature during the adsorption and desorption phases is important and a thermal linking strategy may be required for the bed design. The plateau pressure at 25°C for a $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy is 50 kPa. Because the process is sensitive to temperature, achieving a plateau pressure closer to the 14.2 kPa PPA effluent gas pressure (12.2 kPa H_2 partial pressure) can be obtained by operating at a lower temperature range. Absorption at 12°C is estimated at the PPA H_2 pressure condition if a $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy is assumed to behave similarly to a LaNi_5 alloy evaluated by earlier work.³⁶ Desorption may occur at 25°C or a suitable temperature to meet interface requirements for the recycled H_2 .

V. Conclusion

The 3rd Generation Plasma Pyrolysis Assembly demonstrated targeted performance in stand-alone testing resulting in more than 90% conversion of methane and more than 60% recovery of hydrogen at a 4-crew member processing rate. Minor modifications to the operational parameters of the system could result in modest improvements in performance including an increase in conversion to acetylene over ethylene and a decrease in energy inefficiency. Performance of the 3rd Generation PPA when integrated with a Sabatier system showed a decrease in total methane conversion and hydrogen recovery. Significant quantities of carbon monoxide were formed during the process, resulting in an overall decrease in performance of the system. Improvements to the performance of the system when operating as an integrated unit will be essential to future trade analyses. These improvements may include adjustments

to microwave power and tuning among others. A technical challenge to separate H₂ from the PPA effluent gases has been described. Techniques for separating hydrogen from other gases were reviewed and two approaches—metal hydride separation and solid polymer electrolytic separation—were determined to be the most compatible with the PPA effluent gas conditions. Metal hydride separation was evaluated in more detail. Considerations such as kinetics, operating temperature and pressure, durability, and susceptibility to poisoning were evaluated. An H₂ separator based on a LaNi_{4.8}Sn_{0.2} alloy was evaluated on a preliminary basis. The separator is expected to operate through three stages consisting of an absorption stage, a desorption stage, and a conditioning stage. The conditioning stage will expose a desorbed bed to space vacuum at elevated temperature to regenerate the metal hydride alloy. The process will operate between 10 °C and 25 °C and at a pressure between 10 kPa and 50 kPa. The three metal hydride fixed beds must be engineered for efficient heat transfer during the absorption and desorption stages to handle the exothermic heat of adsorption and promote the endothermic desorption process. The thermal design must be capable of efficiently removing 161 watts from the absorbing bed and supplying a similar thermal load to the desorbing bed. Bed design should consider incorporating thermal linking techniques to promote efficient energy use. The absorption stage will last one hour as will the desorption stage. The conditioning stage will vacuum anneal the metal hydride alloy to reverse poisoning effects on reversible H₂ capacity. The preliminary mass estimate for the basic system is approximately 11 kg; however, mass growth may occur as the design matures. A final mass <20 kg is considered.

Acknowledgments

The authors would like to acknowledge the Advanced Exploration Systems Advanced Resource Recovery and Environmental Monitoring project for funding this effort. Special thanks goes to Jacobs Engineering for technician support in moving, building, modifying, and remodeling the PPA test stand. Particular recognition goes to Mr. Tom Williams for software support.

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